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High-speed spinning of ultra-high molecular weight polyethylene fibres

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Chapter 8

HIGH-SPEED SPINNING OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE FIBRES: EFFECTS OF TEMPERATURE

8.1 Summary

High-speed fibre spinning experiments were performed with solutions of ultra-high molecular weight polyethylene (UHMWPE) in paraffin oil, extruded at various temperatures into a spinline-oven at various temperatures, in order to investigate the influence of temperature on the high-speed spinning process and the properties of the as-spun filaments. It was found that an increase of the extrusion temperature led to an improvement of the maximum winding speed, but reduced the tensile properties, the fraction fibrillar material, the melting temperature and the phase transition temperature of the fibres. This led to the conclusion that the molecular slip increased with temperature, which reduced the effectivity of the stretching of the spinline. Experiments on the cooling of the spinline seemed to corroborate this conclusion. At low extrusion temperatures, however, elastic fracture of the fibres occurred. Optimum fibre properties ($\sigma = 2.8$ GPa, $E = 70$ GPa, $\varepsilon_b = 5.5\%$) were found at an extrusion and spinline-oven temperature of respectively 180°C and 160°C .

8.2 Introduction

In a recent article [1] it was shown that strong fibres can be spun from viscoelastic solutions of ultra-high molecular weight polyethylene (UHMWPE) at high speeds, in a one step procedure. It was found, however, that the long chain molecules made the solutions extremely elastic, which affected the stability of the extrudate and the properties of the fibres [2]. The elasticity of the spinning solution is affected, amongst others, by the molecular weight of the polyethylene, its concentration in the spinning solution, and the extrusion temperature. This article, in which the effect of the temperature of the spinning solution and the spinline-oven is studied, is the third part of a series of three. In the first part the effect of the polyethylene's molecular weight was investigated [3], and in the second part the effect of the UHMWPE concentration in the spinning solution [4] was examined.

The temperature of the spinning solution influences the solvent quality and viscosity [5] and the molecular mobility of the UHMWPE molecules. This affects the rate of

slippage of the entangled molecules in the flowing solution, which counterbalances the effect of the elongational flow in the spinline, in which the molecules are stretched. According to Marrucci [6], the molecules become extended when the product of the rate at which they are elongated ($\dot{\epsilon}$) and their relaxation time (τ) is larger than a constant in the order of unity: $\dot{\epsilon} \times \tau \geq 1$. The relaxation time, however, is inversely proportional to the temperature [7,8], which means that at a higher temperature a higher elongation rate is required to stretch the molecules.

This is consistent with the findings of several spinning [9] and hot-drawing experiments [10,11], in which the drawing was found to be less effective [12] and higher maximum draw(down) ratios could be obtained when the temperature was raised. In spinning experiments it was found that when the temperature becomes very high, the viscosity is reduced to such an extent that capillary failure or draw resonance can occur [13,14]. Odell et al. [15,16] found in flowing dilute solutions of polystyrene that an increase of the temperature reduced the elongation rate at which molecular scission occurred. It was concluded that an increase of the temperature can also reduce the barrier to scission, similar to the molecular fracture mechanism proposed by Zhurkov [17].

An extremely important, temperature related, phenomena that takes place during spinning is the crystallization of the polymer in the spinline. Many excellent studies by Katayama [18], Ziabicki [19,20], Schultz [21], Spruiell [22,23,24], Cuculo [26], Abhiraman [27,28], and Shimizu [29], have found that the crystallization of the polymer in the spinline is stress induced [30,...,33]. This was concluded from facts like the presence of orientation in the spinline previous to crystallization [18,25,28], a shift of the neck towards the die and of the crystallization temperature towards higher values [23,24,31] and an increase in the fibres crystallinity upon increasing the winding speed [18], and the fact that the residence time of the molecules in the spinline is far too short for quiescent crystallization [21,28,34]. George et al. [35] found that the stress at the crystallization point is related to the properties of the as-spun filaments [24,32,36]. This could be related to the orientation of the amorphous material, which, according to others, is strongly correlated to the tensile properties of the fibres [37].

It was recognized that the cooling conditions strongly influence the properties of the as-spun fibres. Many experiments were performed in which the crystallization of the spinline was influenced by isothermal chambers and heated shafts [19,21,38,...,42]. In the case of poly(ethylene terephthalate), a slowly crystallizing polymer, these devices succeeded in giving the polymer enough mobility to form crystals, and fibres with a higher crystallinity and better mechanical properties were obtained. Others increased the cooling rate in order to obtain a more amorphous fibre for texturing

purposes [43]. In the case of the quickly crystallizing polyethylene, however, a spinline-oven was used in order to prevent premature crystallization and obtain higher winding speeds, which led to a better alignment of the molecules previous to crystallization and improved the fibre properties [1]. Skillfull adjustment of the cooling conditions was also found to reduce the differential birefringence, between the fibre's skin and core, which prevented premature filament breakage [39].

Most recently, experiments are performed with combinations of cooling and heating of the spinline [38], and controlling the spinline temperature with liquid isothermal baths [44,45]. It is also recognized that the residence time of the polymer in the hot part of the spinline influences the molecular elongation at the crystallization point. Therefore, the length of the heating device is also an important parameter [41].

In the first part of this series of articles on the effect of the elasticity of the spinning solution on the high-speed spinning process and the properties of the as-spun fibres, it was found that molecular slip has to be prevented in order to obtain high fibre properties, which was confirmed in the second part. However, it was also found that too less molecular slip leads to premature elastic failure of the spinline. An optimum between molecular slip and scission was found at a concentration of 1.5 wt% of the UHMWPE with the highest molecular weight. In this study, the temperature was varied, in order to investigate whether the balance between molecular slip and scission can be further optimized, and some experiments on the influence of the cooling rate in the spinline were performed. For high-speed spinning of UHMWPE fibres optimum fibre properties ($\sigma = 2.8$ GPa, $E = 70$ GPa, $\epsilon_b = 5.5\%$) were found at an extrusion and spinline-oven temperature of respectively 180°C and 160°C.

8.3 Experimental

The used polyethylene, paraffin oil, anti-oxidant and the preparation of the spinning solution, as well as the spinning apparatus, the spinline-oven and the winder were described in chapter 2. The length of the spinline-oven was increased, by inserting a 50 cm long brass pipe in the oven, and heating the part of the pipe that stuck out of the oven by band heaters that were wrapped around it. Another oven was used, which consisted of a 1 m long brass pipe with a diameter of about 15 cm, which was also heated by band heaters. Isolation material was wrapped around both the pipe and the band heaters. The as-spun fibres were extracted at constant length in n-hexane and subsequently dried at 50°C in vacuo. A description of the tensile tests and the DSC and SEM experiments can also be found in chapter 2.

8.4 Results and discussion

The temperature of the spinline is influenced by its diameter, the temperature of the extrudate and the temperature and length of the spinline-oven. This paragraph is divided over two sections. In the first section the influence of the extrusion temperature on the fibre properties is studied and optimized. In the second section some preliminary experiments were performed on the cooling of the spinline, by variation of the temperature of the spinline-oven and its length, and by variation of the diameter of the die.

3.1 Variation of the extrusion temperature

The results of experiments on the effect of the molecular weight of the ultra-high molecular weight polyethylene, and its concentration in the spinning solution, showed that optimum tensile properties were obtained when an UHMWPE is used with $M_w = 5.5 \times 10^6$ kg/kmol and $M_n = 2.5 \times 10^6$ kg/kmol [3], which was dissolved in paraffin oil at a concentration of 1.5 wt% [4]. Several of these spinning solutions were made and extruded at 5 m/min, through a die with a nearly hyperbolical geometry and an exit diameter of 0.5 mm [2], at various extrusion temperatures, while the temperature of the spinline-oven was maintained at 160°C.

At high extrusion temperatures and low winding speeds, the spinline is very sensitive to air turbulences and the fibres, that are wound on top of each other, tend to stick together. This suggests that the molecules in the spinline were not crystallized when they reached the surface of the winder. Upon increasing the winding speed, the sensitivity of the spinline to air turbulences and the tendency of the fibres to stick together is reduced, suggesting that the point of crystallization shifts upwards along the spinline when the winding speed is increased [23,24,31]. When the winding speed is increased, the fracture frequency of the spinline is also increased, due to an increase in spinline tension [32]. This indicated that the lifetime of the spinline depends on the stress that is exerted on it. The same is found when the extrusion temperature is reduced.

When the extrusion temperature is reduced down to 160°C, elastic turbulences appear and the spinline becomes unstable. Apparently, at this temperature the spinning solution is so elastic that the molecules become elongated in the die at an extrusion velocity of 5 m/min [2]. At an extrusion temperature of 160°C the extrusion rate had to be reduced to 1 m/min, in order to obtain a stable extrudate.

Figures 1 and 2 show respectively the tensile strength and the Young's modulus of the fibres, that were spun at 160°C, 180°C and 240°C, as a function of their winding

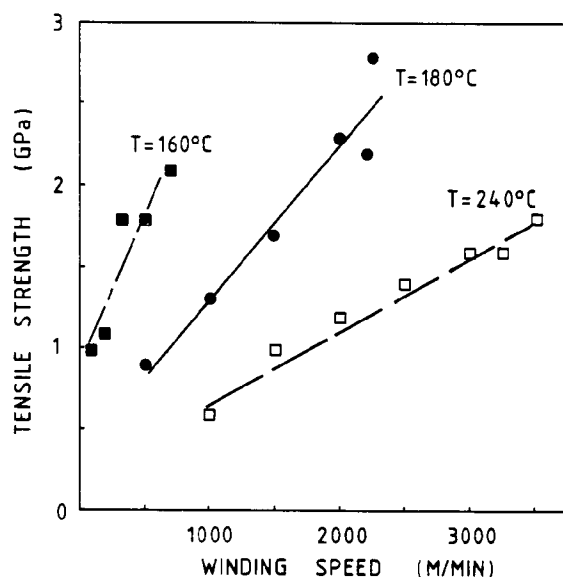


Figure 1: Tensile strength of fibres, that were extruded from a solution of 1.5 wt% UHMWPE in paraffin oil through a die with a nearly hyperbolical shape and an exit diameter of 0.5 mm, at ■ 1 m/min and 160°C, ● 5 m/min and 180°C, and □ 5 m/min and 240°C, as a function of winding speed. The temperature of the spinline-oven was 160°C.

speed. Tensile properties of fibres, that were spun at 190°C and 220°C, lie in between the properties of the fibres, that were spun at 180°C and 240°C, and were omitted for reasons of clarity. These figures show that the tensile properties of the as-spun fibres increase with winding speed, at a constant temperature, and decrease with temperature, at a constant winding speed. It was also found that the maximum winding speed increases with extrusion temperature, and that the maximum tensile properties have an optimum at an extrusion temperature of 180°C. This is also shown in figure 3, together with the data found at various other extrusion temperatures.

Since the tensile properties of the as-spun filaments depend on the molecular elongation in the spinline, it is concluded from these figures that the molecular strands between entanglements in the spinning solution become elongated upon stretching the spinline, and that this elongation is counterbalanced by relaxation at high extrusion temperatures. This is consistent with the findings of Hoogsteen et al. [46]. It is supposed that relaxation takes place by molecular slip of the strands

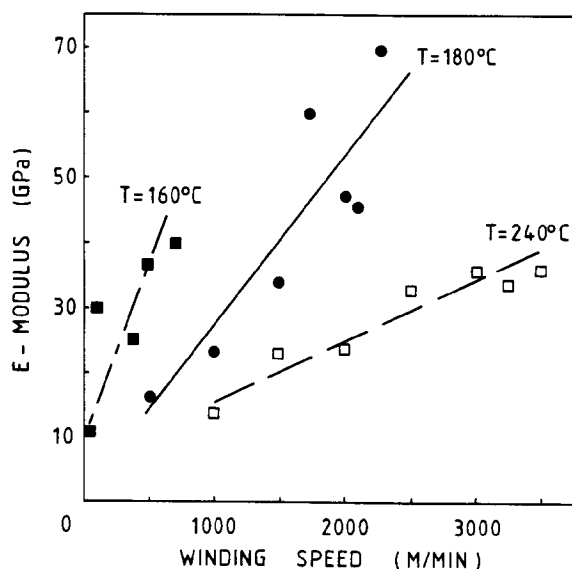


Figure 2: Young's modulus of the fibres, mentioned in figure 1, as a function of their winding speed.

through their entanglement junctions, as well as fracture of some of the molecular strands at a thermally reduced barrier to scission [15,16]. When the temperature is high, the molecular mobility is high, and most of the molecules can slip through their entanglement hooks at high rates, while some of them fracture. This is consistent with the observed increase in maximum winding speed, when the temperature is raised.

At low temperatures the molecular slippage is reduced and the spinning solution becomes more elastic. The molecular strands between entanglements become elongated already at low stretch ratios of the spinline, or in the flow field in the die [2]. This explains why the tensile properties of the fibres that were spun at low temperatures, are higher than the properties of the fibres that were spun at high temperatures at the same winding speed. Fracture of the molecular strands between entanglements will appear when these strands become completely elongated [15,47]. When molecular slip is reduced, this will happen at low elongation ratios of the spinline, which is consistent with the low maximum winding speed that was found at low extrusion temperatures. The maximum tensile properties ($\sigma = 2.8$ GPa, $E = 70$ GPa, $\epsilon_b = 5.5\%$), were found at an extrusion temperature of 180°C . This temperature probably is an optimum temperature between molecular slip and molecular scission [13,48]. Termonia et al [11] have called this a temperature window of deformation.

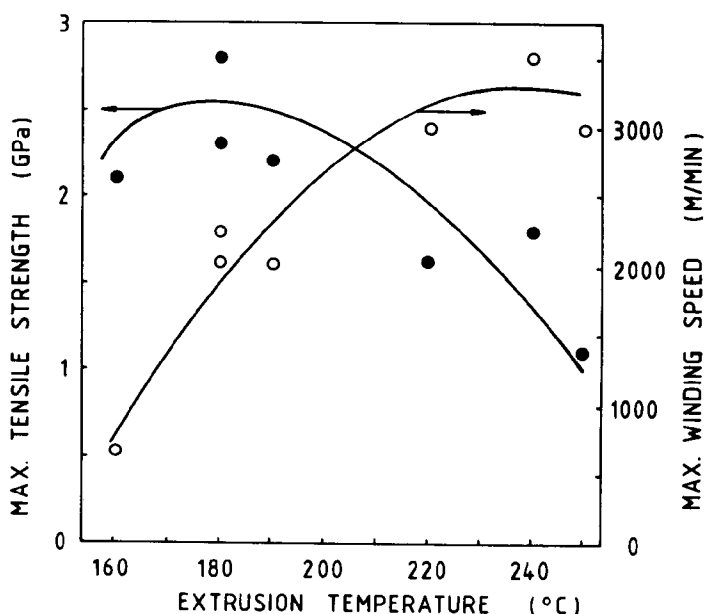


Figure 3: Maximum obtainable tensile strength and winding speed, of fibres spun from 1.5 wt% UHMWPE solutions, as a function of the extrusion temperature. The temperature of the spinline-oven was 160°C. The extrusion rate was 5 m/min, except for the fibres that were extruded at 160°C, in which case it was 1 m/min.

Figures 4 a and b present SEM micrographs of fibres, that were spun at an extrusion temperature of 180°C at 5 m/min, and wound at respectively 500 and 2250 m/min. During spinning long fibrillar entities must have been created, that crystallized after extension in the spinline as shish-kebab structures. The SEM micrographs clearly show that the dimensions of the shish-kebabs decrease with winding speed, and that the fibrils between the 'kebabs' are not elongated. When the winding speeds are high, the oil is squeezed out of the fibres (syneresis) and the shish-kebabs are pulled so tight against each other, that their dimensions are difficult to distinguish. The shish-kebab dimensions are presented in table 1, which shows that the extrusion temperature does not affect the shish-kebab dimensions. Apparently, the shish-kebab dimensions are controlled by the stress in the spinline rather than by its temperature. This seems to be similar to experiments performed by Kobayashi et al. [49], who found that shear stress enhances the crystal nucleation and growth, which increases the number and decreases the size of the crystals.

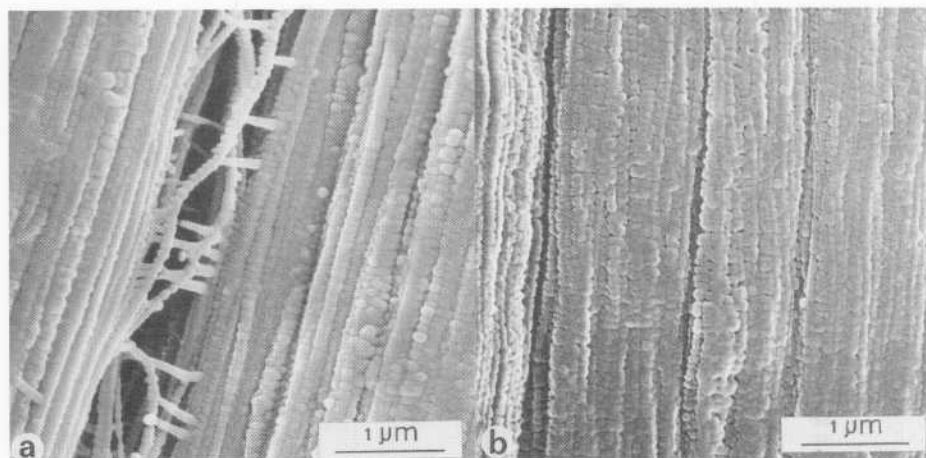


Figure 4: SEM micrographs of representative details of fibres, that were extruded at 180°C at 5 m/min, and wound at a) 500 m/min, and b) 2250 m/min.



Figure 5: WAXS diffraction patterns of fibres, that were extruded at 180°C at 5 m/min, and wound at a) 500 m/min, and b) 2250 m/min. The fibre axis is vertical.

Table 1: Dimensions of the shish-kebab structures, as determined with SEM.

extrusion temperature (°C)	winding speed (m/min)	'kebab' thickness (nm)	'kebab' width (nm)
180	500	49-100	135-270
180	1000	36-90	75-160
180	1500	35-71	71-125
180	2250	35-54	70-140
170	1000	43-80	90-150
180	1000	36-90	75-160
190	1000	50-110	80-160
220	1000	50-100	90-170

Wide angle X-ray scattering experiments (WAXS) were performed, in order to investigate whether the stretching of the spinline improves the molecular orientation, and whether an increase in extrusion temperature reduces the orientation. Figures 5 a and b present the WAXS diffraction patterns of fibres, that were extruded at a temperature of 180°C at 5 m/min and wound at respectively 500 and 2250 m/min. They show that the orientation of the crystals in the fibres increases with winding speed. However, fibres that were spun at other temperatures show similar WAXS diffraction patterns. No effect of the temperature on the crystal orientation could be found. Obviously, WAXS experiments cannot provide information on the molecular slip. Probably the molecular slippage affects the crystal size and the amorphous orientation rather than the crystal orientation.

In unconstrained DSC experiments the crystallinity of the fibres was determined, and presented as a function of winding speed in figure 6. It was found that the crystallinity of the fibres was independent of their winding speed, as was found before [3,4]. Apparently, the higher quench rate at higher winding speeds did not reduce the crystallinity of the fibres. The size of the crystals, however, was influenced by the winding speed, as can be concluded from the rise in peak melting temperature with winding speed, that is found in figure 7. According to the Gibbs-Thomson relation [50] the peak melting temperature of a crystal is related to its size. Since the melting temperature of the fibres increases when the winding speed is raised, it is concluded that the crystals grow in size upon elongation of the spinline, which is consistent with literature [18,...,33]. It was concluded that the crystallization of the molecules in the spinline is stress induced. Figure 7 shows that the melting temperature of the as-spun

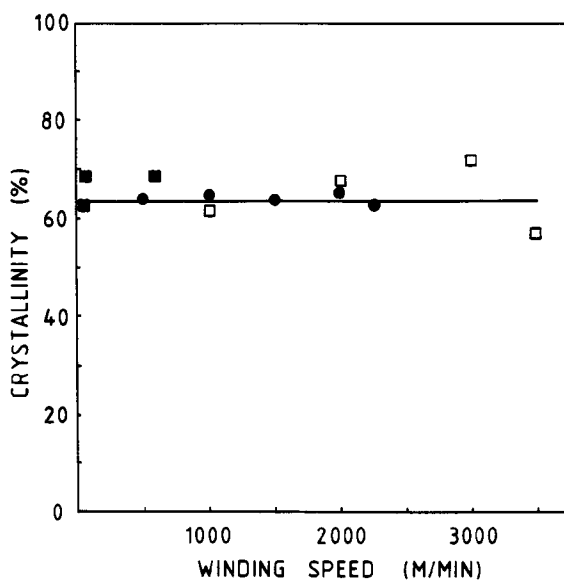


Figure 6: Crystallinity, as measured with DSC, of fibres that were extruded at ■ 1 m/min at 160°C, ● 5 m/min at 180°C, and □ 5 m/min at 240°C, as a function of their winding speed.

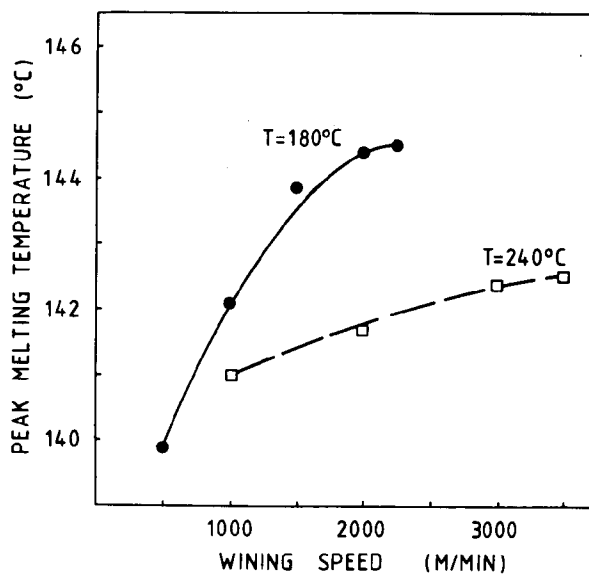


Figure 7: Peak melting temperature, as measured with DSC, of fibres that were extruded at 5 m/min at 180°C and 240°C, as a function of winding speed.

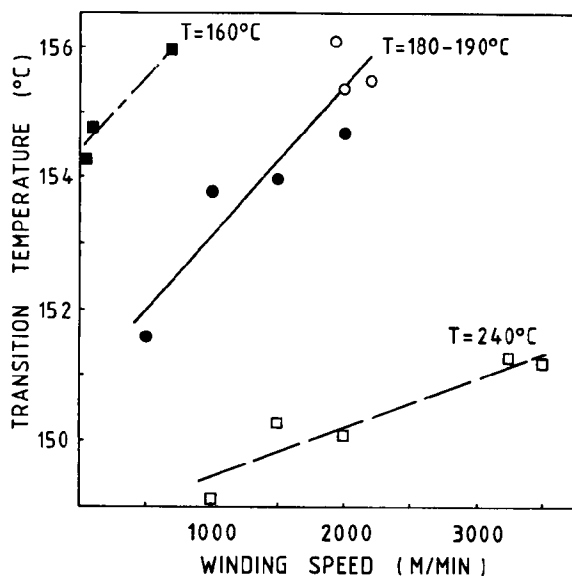


Figure 8: Orthorhombic to hexagonal phase transition temperature, as measured in constrained DSC experiments, of fibres that were spun at ■ 1 m/min at 160°C, and at 5 m/min at ○ 180°C, ● 190°C, and □ 240°C, as a function of winding speed. The temperature of the spinline-oven was 160°C.

fibres is reduced when the extrusion temperature is raised from 180°C to 240°C. The increase in extrusion temperature apparently reduces the stress in the spinline.

In constrained DSC experiments in which paraffin oil is added to the fibres [1], the orthorhombic to hexagonal phase transition temperature [51,52] of the UHMWPE fibres is found. This phase transition temperature is thought to be connected to the size of the crystals in the fibrils, and since the crystals probably grow mainly uniaxially when the transient entanglement network is stretched, it is thought to be connected to the length of the fibrillar crystals [53,54]. Figure 8 shows that the phase transition temperature increases with the speed at which the fibres were wound, which is consistent with the hypothesis that the molecules become stretched to a higher extent, and form longer crystals upon cooling, when the winding speed increases. Since the shish-kebab dimensions decrease with winding speed, it is concluded that the length of the crystals in the fibrillar backbone is not related to the heart-to-heart distance between the 'kebabs'.

Figure 8 also shows that the phase transition temperature of the as-spun fibres

decreases when the extrusion temperature is raised. This implies that stress relaxation in the spinline decreases the length of the fibrillar crystals. Probably the slip and recoiling of the molecules in the hot spinning solution inhibits the aligning of these molecules, whereupon they form shorter crystals upon cooling.

From the constrained DSC thermograms the amount of fibrillar material in the fibres was estimated [1], and presented as a function of the winding speed in figure 9. This figure shows that the fraction fibrillar material increases with winding speed, similar to the increase in tensile strength. It also shows that at a given winding speed the fraction fibrillar material is high, when the used extrusion temperature was low. When the lines in figure 9 are extrapolated to lower winding speeds, it is found that the fibres that were spun at 160°C, contain fibrils even when the spinline is not stretched. This means that the molecular strands between entanglements are already elongated in the die [2]. This is consistent with the elastic turbulences that were found at 160°C at an extrusion rate of 5 m/min. However, the fibres, that were spun at 240°C, only become fibrillar when the winding speed is higher than about 500 m/min. This implies that the molecules can relax so quickly, that they are not elongated at winding speeds lower than 500 m/min, which means that a considerable amount of molecular slip takes place in this solution.

Figure 10 shows that the tensile strength of the high-speed spun fibres is linearly related to their fraction fibrillar material, and that this relation is valid for any UHMWPE concentration in the spinning solution. The extrusion temperature influences the fibre's tensile strength in the same manner as its fraction of fibrillar material. Probably the molecules, that bear the load in the spinline, are elongated and aligned and crystallize in the fibrils, determine the strength of the as-spun filaments. Upon extrapolation of the line in figure 10, it is found that even the fibres that do not contain fibrils have a tensile strength of about 0.5 GPa. These ductile lamellar fibres are probably cold drawn during the tensile test. Figure 10 shows that even under optimum spinning circumstances the fibres do not become completely fibrillar. At an extrusion temperature of 180°C, an extrusion rate of 5 m/min and a winding speed of 2250 m/min, the fraction fibrillar material in the fibres is 0.55 and their tensile properties are: $\sigma = 2.8$ GPa, $E = 70$ GPa, and $\epsilon_b = 5.5$ %.

3.2 Some experiments on the cooling of the spinline

The stress induced crystallization of the UHMWPE in the spinline seems to determine the properties of the high-speed spun fibres. Variation of the cooling rate [19,21, 38,...42] and the residence time of the molecules in the hot part of the spinline

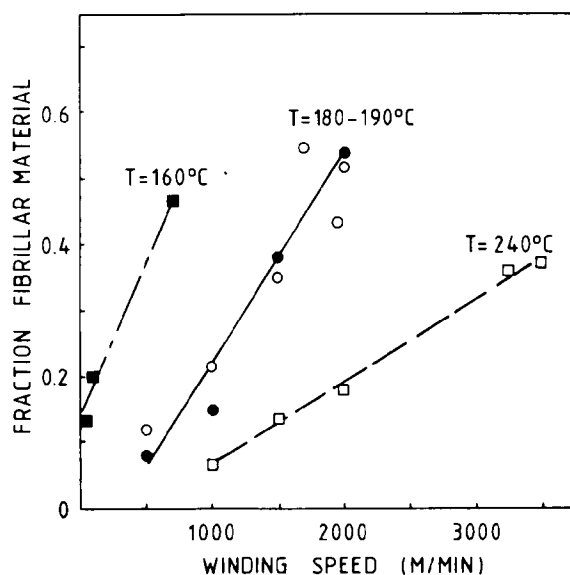


Figure 9: Fraction fibrillar material, of the fibres that were presented in figure 8, as a function of their winding speed. (O = 180°C, ● = 190°C)

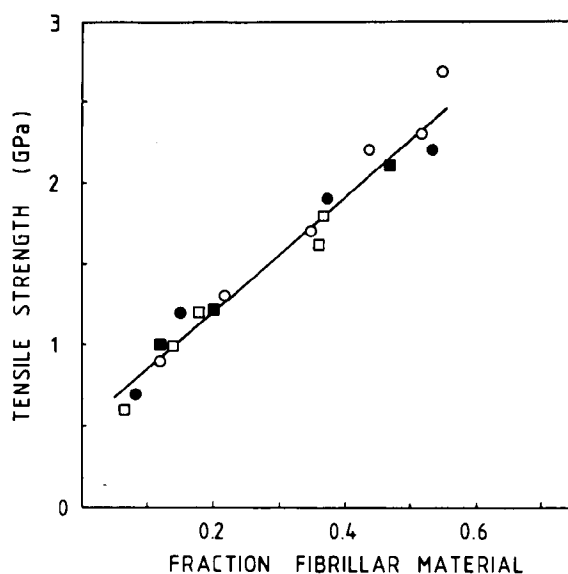


Figure 10: Tensile strength, of the fibres that were presented in figure 9, as a function of their fraction fibrillar material.

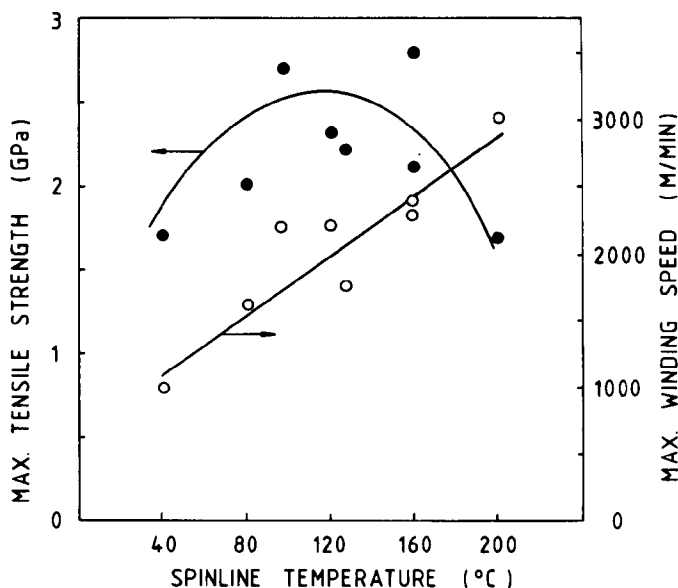


Figure 11: Maximum obtainable tensile strength and winding speed, of fibres spun from 1.5 wt% UHMWPE solutions, at 5 m/min and 180°C, as a function of the temperature of the spinline-oven.

[41] might confirm the abovementioned picture. Some preliminary experiments were performed in which the temperature of the spinline-oven, the diameter of the extrudate, and the length of the spinline-oven were varied. The extrusion temperature was kept constant at 180°C and the extrusion rate at 5 m/min.

It was found that the tensile properties of the as-spun fibres are influenced by the temperature of the spinline-oven, similar to the influence of the extrusion temperature. At a constant winding speed the tensile strength and Young's modulus decrease with increasing temperature of the spinline-oven, and upon raising the temperature, the maximum winding speed increases and the maximum tensile properties go through an optimum. This is shown in figure 11, which is very similar to figure 3. Obviously, the molecular elongation in the spinline is influenced by its temperature, which is controlled by both the temperature of the spinning solution and the spinline-oven. An optimum value of the temperature of the spinline-oven was found at 120-160°C, but it must be noted that this is only valid when the extrusion temperature is 180°C. At other extrusion temperatures, the optimum temperature of the spinline-oven will be shifted to other values.

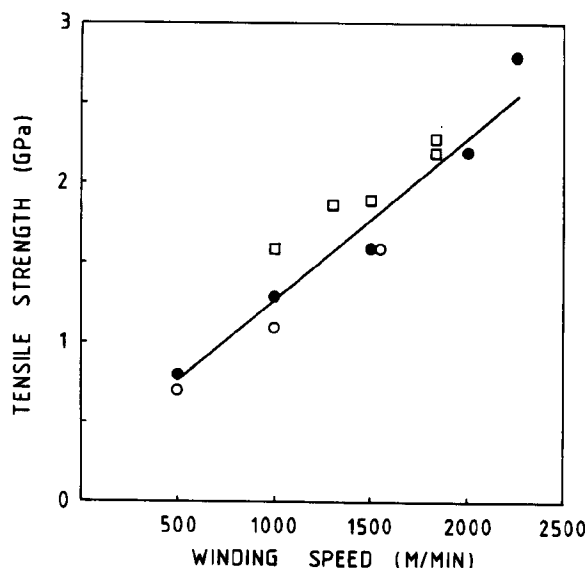


Figure 12: Tensile strength of fibres, that were extruded from a solution of 1.5 wt% UHMWPE at 180°C, into a spinline-oven at 160°C, as a function of their winding speed. The diameter of the die and the extrusion velocities were varied: ● diameter = 0.5 mm, extrusion rate = 5 m/min, ○ diameter = 1.0 mm, extrusion rate = 5 m/min, □ diameter = 1.0 mm, extrusion rate = 1.25 m/min.

The diameter of the spinline also affects its cooling and crystallization. Figure 12 presents the tensile strength of fibres, that were spun using dies with exit diameters of 0.5 and 1.0 mm, as a function of the winding speed. When the volumetric flow is kept constant, the extrusion rate is reduced to 1.25 m/min, and the diameter of the spinline is unaltered. Figure 12 shows that this reduces the maximum winding speed and tensile strength somewhat. This was found before [2], and is thought to be due to overstretching of the spinline.

When the extrusion rate is maintained at 5 m/min, the volume flow is quadrupled, which doubled the diameter of the spinline and retarded the cooling rate of its interior. The length of the hot part of the spinline is now increased, which increases the residence time of the molecules in the elongational flow field. At low winding speeds it was found that the fibres, that were wound on top of each other, tend to stick together, and at high winding speeds the hot fibre was flung away from the winder by the centrifugal forces. Apparently, the spinline was too short to allow the extrudate

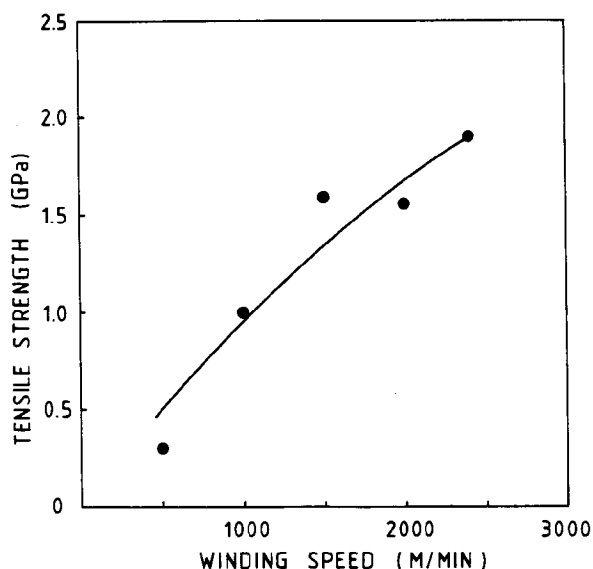


Figure 13: Tensile strength, as a function of winding speed, of fibres, that were extruded from a solution of 1.5 wt% UHMWPE at 2.5 m/min at 230°C through a die with an exit diameter of 1.0 mm, into a spinline-oven with a length of 1 m and a temperature of 160°C. The length of the spinline was 4 m.

to cool down and crystallize, before it reached the winder. In figure 12 the tensile strength of these fibres is compared to the strength of the fibres, that were spun using the die with the 0.5 mm diameter, as a function of the winding speed. It shows that although the maximum winding speed is reduced by increasing the spinline diameter, it does not affect the tensile strength of fibres, that were wound at the same speed. It is highly likely that a film of hot paraffin oil is formed around the spinline by syneresis, which reduces the effect of the cooling rate and diminishes the effect of the diameter variation on the fibre properties.

In order to increase the residence time of the molecules in the hot part of the spinline, the length of the spinline-oven was increased, by inserting a 50 cm long brass pipe in the oven, and heating the part of the pipe that stuck out of the oven. An increase from 20 to 50 cm, however, only reduced the tensile properties of the fibres by a few tenths of GPa, which is within experimental error. Therefore a preliminary experiment was performed in which the spinline-oven was replaced by a 1 m long brass

pipe with a diameter of about 15 cm, which was heated by band heaters that were strapped around it. The length of the spinline was increased to 4 m, the extrusion temperature was 230°C, the temperature of the spinline-oven was 160°C, and the die with the exit diameter of 1.0 mm was used.

At an extrusion rate of 5 m/min, the thick hot spinline was flung away from the winder already at a winding speed of about 1500 m/min, therefore the extrusion rate was reduced to 2.5 m/min. The results of this experiment are plotted in figure 13, which shows the tensile strength of the as-spun fibres as a function of their winding speed. It was found that increasing the length of the hot part of the spinline does not improve the maximum obtainable fibre properties. It seems to give the molecules more time to slip, which confirms the conclusions that were drawn from the experiments on the extrusion temperature.

8.5 Conclusions

In high-speed spinning experiments with solutions of UHMWPE it was found that an increase of the extrusion temperature improves the stretchability of the spinline. The tensile properties of the as-spun fibres, and their fraction fibrillar material and melting and phase transition temperatures, increase with winding speed at a constant temperature, and decrease with temperature at a constant winding speed. From this was concluded that the molecules become elongated in the spinline and crystallize under influence of the stress, and that this orientation is counterbalanced by molecular slip, which increases with temperature. Some preliminary experiments on the cooling of the spinline seem to confirm these conclusions. At low extrusion temperatures, however, elastic failure of the spinline takes place.

The shish-kebab dimensions were found to decrease with winding speed, while the phase transition temperature of the fibres, which is thought to be correlated to the length of the crystals in the fibrils, was found to increase with winding speed. It was concluded that the heart-to-heart distance between the 'kebabs' is not correlated to the crystal lengths in the fibrils. The orientation of the crystals in the fibres, as detected with WAXS, was found to increase with winding speed, but turned out to be unaffected by the extrusion temperature. The crystallinity of the fibres was about 65%, independent of the winding speed and the extrusion temperature.

The tensile properties of the fibres are correlated to their fraction fibrillar material, independent of the temperature at which they were produced. Optimum tensile properties ($\sigma = 2.8$ GPa, $E = 70$ GPa, and $\epsilon_b = 5.5\%$) are found at an extrusion temperature of 180°C, while the temperature of the spinline-oven was 160°C. At these

temperatures, however, the fraction fibrillar material had not reached unity. It was concluded that in order to obtain stronger fibres, the stretching temperature has to be reduced in order to reduce molecular slip, and the elongation rate in the spinline has to be lowered in order to reduce molecular scission. These conditions are best met in a hot-drawing procedure.

8.6 References

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